(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 516 401 A1**

(12) EUROPEAN PATENT APPLICATION

(21) Application number: 92304807.8

(22) Date of filing: 28.05.92

(51) Int. Cl.5: C01B 23/00, C01B 21/04, B01D 53/04

(30) Priority: 30.05.91 US 710190

(43) Date of publication of application: 02.12.92 Bulletin 92/49

(84) Designated Contracting States: BE DE FR GB IT NL

(71) Applicant: THE BOC GROUP, INC.
575 Mountain Avenue
Murray Hill New Jersey 07974 (US)

(72) Inventor: Jain, Ravi
48 Canterbury Court
Piscataway, New Jersey 08854 (US)
Inventor: Tamhankar, Satish S.
2111 Algonquin Drive
Scotch Plains, New Jersey 07076 (US)
Inventor: LaCava, Alberto I.
2201 Orchard Drive
South Plainfield, New Jersey 07080 (US)

(74) Representative: Wickham, Michael et al
c/o Patent and Trademark Department The BOC Group plc Chertsey Road
Windlesham Surrey GU20 6HJ (GB)

(54) Purification of gas streams.

(57) A process for producing a substantially oxygen-free inert gas product such as argon containing not more than one ppm by volume of oxygen and not more than 1 volume per million of water vapour comprises introducing hydrogen into a compressed crude argon gas stream which contains oxygen.

The hydrogen is added at a rate at least sufficient to meet the stoichiometric requirement for reaction with the oxygen impurity to form water vapour. The argon stream passes through a first catalytic reactor 5, in which the oxygen impurity reacts at elevated temperature with hydrogen to form water vapour. The resulting gas stream contains less than 500 vpm of oxygen. It is cooled in a heat exchanger 8 and flows into one of vessels 30 and 32. It first encounters a first layer of adsorbent 34 or 36 effective to remove water vapour therefrom, then a layer of oxidation catalyst 38 or 40 which enables residual oxygen in the argon to react with residual hydrogen to form water vapour, and finally a second layer of adsorbent 42 or 44 effective to remove the water vapour formed in the layer 38 or 40.

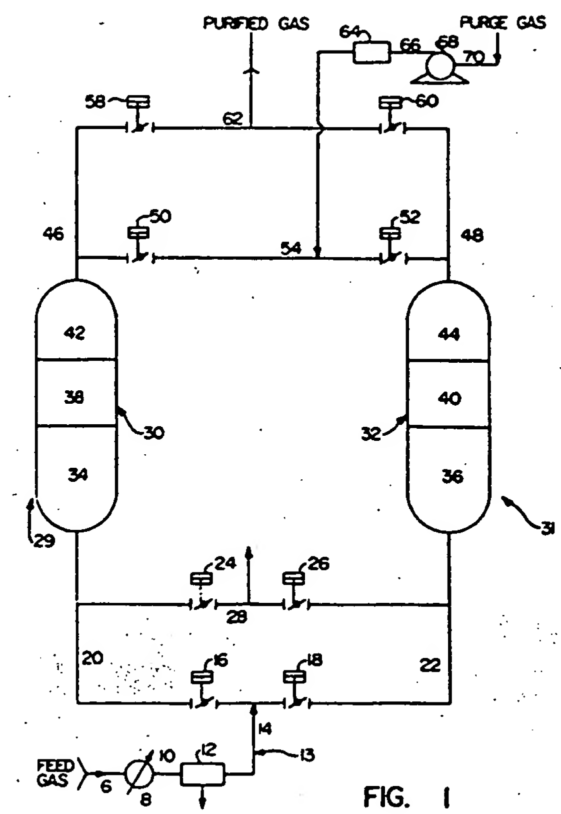

FIG. 1

EP 0 516 401 A1

This invention relates to a method and apparatus for purifying oxygen-containing gas streams. More particularly the invention pertains to a process for producing substantially oxygen-free 'inert' gas streams, such as oxygen-free argon, nitrogen, helium and neon.

Inert gases, such as argon, nitrogen, and the like are widely used in industrial processes such as shielded arc welding, semiconductor manufacture, metal refining, electric light bulb manufacture and inert gas-blanketed chemical processes. In many industrial processes the presence of oxygen as an impurity in the inert gas frequently brings about undesirable results, such as the formation of oxides of materials treated in the process. Accordingly, it is frequently necessary that the inert gases used in these processes be substantially free of oxygen.

Crude inert gases, such as argon and nitrogen, that are separated from air by cryogenic or non-cryogenic means, ordinarily contain up to several percent by volume of oxygen. For example, argon manufactured from air by cryogenic distillation usually contains up to 3% oxygen. This happens because it is very difficult to separate oxygen completely from argon by cryogenic distillation, since argon and oxygen have very close boiling points. When it is desired to produce substantially oxygen-free argon from oxygen-containing sources such as air, it is generally necessary to resort to purification processes other than cryogenic distillation. Methods for manufacturing high purity oxygen-free argon and other high purity inert gases include adsorption by means of molecular sieves, and catalytic deoxygenation (oxygen-removal) processes, such as the catalytic oxidation of oxygen- and hydrogen-containing streams and chemisorption of the oxygen by getter materials. Catalytic processes are generally preferred over adsorption because they provide superior results and have low operating costs.

A preferred catalytic process for the removal of oxygen from gas streams involves adding hydrogen to the gas stream and subsequently contacting the gas stream with an oxidation catalyst, for example, a noble metal catalyst, such as platinum or palladium. The catalyst converts the oxygen and hydrogen into water, which can be subsequently removed. Such a process is disclosed in US Patent No 4,960,579, which teaches the production of high purity nitrogen from air by first separating nitrogen from air by membrane separation or pressure swing adsorption and then removing residual oxygen from the nitrogen product by introducing purified hydrogen into the gas stream and contacting the stream with an oxidation catalyst such as a noble metal or combination of noble metals to cause the oxygen and hydrogen in the stream to combine to form water. Other patents which disclose contacting oxygen- and hydrogen-containing gas streams with a deoxygenation catalyst are US 3,535,074, 4,579,723 and 4,713,224.

This above-described catalytic deoxygenation process performs satisfactorily with fresh catalyst; however the concentration of oxygen impurity in the product gas can increase over extended periods of time. It appears that the catalyst gradually deteriorates upon continued usage. (We postulate that the deterioration of the catalyst may be caused by the presence of moisture or catalyst poisons that are present in the gas stream being treated. These impurities may come from various sources. One possible source of impurities is the gas stream entering the system for purification. This stream may contain trace amounts of gaseous impurities, such as sulphur compounds. Another possible source of impurities is the water that is used to cool a feed gas compressor commonly used to take for purification impure product gas, such as argon, from a rectification column of an air separation plant. The cooling water may contain elements or compounds, such as chlorine or compounds of chlorine, phosphorus and molybdenum that are initially present in the water or that are added in water treatment operations. The above impurities are known catalyst poisons. Even though they are present in the gas stream in very small concentrations, long term exposure of the deoxygenation catalyst to them will slowly cause the catalyst to become poisoned. In addition to catalyst poisons, moisture present in the gas stream may cause a reduction of the oxidation activity of the catalyst.)

It is an aim of the invention to provide a process and apparatus which are able to ameliorate the above-described problem.

According to the invention there is provided a process for the removal of oxygen from an inert gas stream containing oxygen impurity comprising:

a) introducing hydrogen into the inert gas stream to the extent necessary to ensure that the gas stream contains at least sufficient hydrogen to enable all of the oxygen in the gas stream to be converted to water;

b) contacting the inert gas stream with an oxidation catalyst in a first catalysis zone, thereby reacting a substantial amount of the oxygen in the stream with hydrogen to form water;

c) cooling the gaseous effluent from said first catalysis zone;

d) contacting the cooled gaseous effluent with an adsorbent in a first adsorption zone, thereby removing substantially all of the water contained in the cooled gaseous effluent characterised by

e) contacting the substantially anhydrous effluent from said first adsorption zone with an oxidation catalyst in a second catalysis zone, thereby combining substantially all of the oxygen in said substantially anhydrous effluent with hydrogen to produce water; and

f) contacting the gaseous effluent from said second catalysis zone with an adsorbent in a second adsorption zone, thereby producing a purified gas stream containing not more than about 1 vpm of oxygen, and not more than about 1 vpm water.

The invention also provides apparatus for purifying an inert gas stream including oxygen impurity, comprising:

(i) a first catalytic reaction zone for reacting the oxygen impurity in the inert gas stream with hydrogen to form a partially purified gas stream comprising said inert gas, residual oxygen impurity and water;
(ii) means for cooling the partially purified inert gas stream; and
(iii) a first adsorption zone for adsorbing said water from the cooled gas stream;

characterised in that the apparatus additionally includes downstream of said adsorption zone;

(iv) a second reaction zone for reacting with hydrogen the residual oxygen in the partially purified inert gas stream to form water; and
(v) a second adsorption zone for adsorbing water formed in the first reaction zone, whereby a purified inert gas stream essentially free of water vapour and oxygen is able to be produced.

The first and second adsorption zones preferably contain one or more beds of an adsorbent for moisture and other gaseous impurities that are harmful to the oxidation catalyst. The adsorbents may be any substances that adsorb water and the above-described gaseous impurities. Preferred adsorbents include activated alumina, silica gel, zeolites and combination thereof. The catalysis zones each contains one or more catalysts that catalyse the conversion of oxygen and hydrogen to water. Any catalyst that will effect the desired reaction may be used. Preferred oxidation catalysts for the second zone are supported palladium and supported mixtures of palladium and platinum.

The relative thicknesses of the adsorption and catalyst beds may be varied to suit the conditions encountered in the process. In some cases, such as when the effluent gas from the first catalysis zone contains small concentrations of oxygen and relatively large concentrations of moisture or other gaseous impurities, it may be preferable that the first adsorption bed be large relative to the second adsorption bed, because relatively small amounts of water will be generated in the second catalysis zone.

The process according to the invention can be conducted either batchwise or continuously. In either case, the treatment region containing the two adsorption zones and the catalysis zone is periodically regenerated by purging and hence removing the accumulated adsorbed impurities. In a batchwise system, purification of the feed gas must be stopped during regeneration of the treatment section. In the continuous system, which is the preferred embodiment, a plurality of treatment regions are used, with at least one treatment region producing purified gas while at least one other treatment region is undergoing regeneration. Regeneration of the treatment regions may be carried out by purging with a suitable gas at near feed temperatures in a pressure swing mode or at elevated temperatures in a temperature-swing mode.

After the product gas leaves the treatment region unreacted hydrogen can be removed from the product gas by a separation treatment, such as cryogenic distillation. When the feed gas is an argon stream that contains small amounts of nitrogen, which may be the case with crude argon produced by cryogenic air separation, the residual nitrogen can also be removed by the cryogenic distillation used for hydrogen removal subsequent to treatment by the process of the invention.

In a preferred embodiment the feed gas is purified in a single vessel containing three contiguous sections: a first moisture adsorption section, a catalysis section and a second moisture adsorption section.

The term 'inert gas' as used herein includes nitrogen within its scope.

The method and apparatus according to the invention are particularly suited for the purification of a crude argon stream typically including up to about 3% by volume of oxygen impurity. Such crude argon streams are produced commercially in some processes in which air is separated by (fractional) distillation.

The first catalysis zone is preferably operated such that most of the oxygen impurity reacts in such zone with the hydrogen. Preferably the gas stream leaving the first catalysis zone contains no more than 500 volumes per million of residual oxygen. Typically, therefore, the whole of the stoichiometric requirement of the process for hydrogen is provided upstream of the first catalysis zone.

The process according to the invention provides a number of advantages over known processes. Passing the feed gas through an adsorbent bed prior to contacting it with the oxidation catalyst in the second catalysis zone removes substances from the gas that tend adversely to affect the catalyst, thereby prolonging the life of the catalyst. Purging the adsorption and catalysis sections with a gas that is substantially free of oxygen and moisture regenerates the beds and enables the catalyst to continue to perform at high efficiency. When the effluent gas from the first catalysis zone contains no more than about 500 vpm oxygen, as in a preferred embodiment, the second catalysis zone can be operated at a relatively low temperature, thereby minimising the chance of inadvertently desorbing the adsorbent beds.

The process and apparatus according to the invention will now be described by way of example with ref-

erence to the accompanying drawings, in which like reference numerals are used in the various figures to designate like parts, and in which:

FIGURE 1 is a schematic view of one embodiment of the invention, showing a continuous process for the production of highly purified gas utilising either a pressure-swing or a temperature-swing mode of operation; and

FIGURE 2 is a schematic view of a variation of the embodiment shown in FIGURE 1, showing subsequent treatment of the highly purified gaseous product in a cryogenic distillation system.

FIGURE 3 is a schematic view showing another variation of the embodiment illustrated in FIG. 1.

Referring to Figures 1 and 2 of the drawings, a gas stream enters the illustrated apparatus at a pressure of 50 to 150 psig through a line 6. The gas stream is formed by taking a crude argon product, typically containing from ? to 3 by volume of oxygen impurity, and a small amount of nitrogen impurity, from a rectification column (not shown) of an air separation plant (not shown) in which column argon is separated from oxygen. The crude argon stream is compressed in a compressor (not shown) to bring it to a chosen pressure in the range of 50 to 150 psig. Hydrogen is then added to the crude argon stream at a note such that the resulting gas mixture contains the stoichiometric quantity of hydrogen required to react with all the oxygen impurity, or a quantity of hydrogen slightly in excess of this stoichiometric quantity. The resulting mixture of argon, hydrogen and oxygen is then passed through a first catalytic reactor (not shown) in which the hydrogen reacts with the oxygen impurity to form water vapour. The first catalytic reactor, and its operation, are essentially the same as in a conventional argon purification unit. Typically, the reaction between hydrogen and oxygen does not go to completion, particularly if the catalyst is beginning to age. Accordingly, the gas stream entering the line 6 typically contains up to 500 volumes per million of residual oxygen impurity, and a corresponding quantity of residual hydrogen. The argon stream is also at elevated temperature when it enters the line 6. It is then sent to a heat exchanger 8, or other cooling means, in which it is cooled an is introduced via a line 10 into a water separator 12 (also optional) to remove entrained drops of liquid water therefrom. The gaseous feed enters a line 14 and is generally at a temperature of from about 5°C to about 70°C, and preferably at a temperature of from about 10°C to about 50°C. Heat exchanger 8 and water separator 12 are preferably used when the incoming gas stream contains significant quantities of water vapour. Removing some of the moisture from the feed stream in separator 12 lightens the burden on a downstream water adsorption zone described hereinbelow.

If the feed gas does not contain sufficient hydrogen to consume all of the oxygen contained in the gas stream by combination therewith to form water, additional hydrogen can be injected into the feed gas stream through line 13. The amount of hydrogen injected into the gas stream depends upon the amount of oxygen and hydrogen present in the stream. The amount of hydrogen added is such that the total amount of hydrogen in the gas stream will be at least the stoichiometric quantity required for the conversion of substantially all of the oxygen present in the feed stream to water. Preferably, a stoichiometric excess of hydrogen is added to ensure that all of the oxygen present in the stream is consumed.

The hydrogen-containing feed gas stream next enters treatment zone 29 or treatment zone 31. The treatment zones may be operated in a temperature swing mode (as shown in Figure 1) in which water is adsorbed at a lower temperature in a bed of adsorbent and the bed then regenerated by subjecting it to a higher temperature, or in a pressure swing mode in which water is adsorbed at a higher pressure in a bed of adsorbent and the bed then regenerated by subjecting it to a lower pressure. The specific zone which the feed gas enters depends on which phase of the operating cycle the system is in. The description of the operation of the system will begin with the system in the phase in which treatment zone 29 is in the gas purification mode and treatment zone 31 is in the regeneration mode.

For the temperature-swing embodiment shown in FIG. 1, with vessel 30 in the purification mode and vessel 32 in the regeneration mode, vessel 30 is normally pressurised slowly with feed gas prior to the start of the purification process. Valve 16 is open for the pressurisation of vessel 30. After pressurisation of vessel 30, pressurised feed gas is admitted to treatment zone 29, comprising vessel 30, through line 14, valve 16 and line 20. Vessel 30 comprises three contiguous sections, first adsorption section 34, catalysis section 38, and second adsorption section 42. The physical separation of the three sections of treatment vessel 30 is effected by means well known in the art. For example, catalysis section 38 may be separated from adsorption sections 34 and 42 by a stainless steel screen.

First adsorption section 34 contains at least one layer of an adsorbent material which is capable of adsorbing all of the water and any catalyst poisoning impurities contained in the gas stream. Suitable adsorbents include activated alumina, silica gel, zeolites and combinations thereof. Preferably, adsorption section 34 comprises a predominant layer of activated alumina or silica gel and a layer of zeolite, for example, zeolite 13X or 5A. The water and other catalyst poisons are removed from the gas stream to prevent deactivation of the oxidation catalyst contained in catalysis section 38. When the process is carried out at low temperatures it is particularly important to prevent moisture from contacting the catalyst bed since in doing so it tends to deposit on

the catalyst, thereby forming a barrier over the catalyst and preventing the oxygen and hydrogen reactants from contacting the catalyst.

The gas stream next passes through catalysis section 38 of treatment vessel 30. Catalysis section 38 contains catalysts for the conversion of hydrogen and oxygen to water. The catalysts used in the invention may be any element or compound or mixture of elements or compounds that will catalyse the reaction of hydrogen and oxygen to form water. Preferred oxidation catalysts are catalysts containing noble metals, such as platinum, palladium, rhodium or mixtures of these, either alone or in combination with other metals. The catalyst is preferably mounted on an inert support, such as alumina.

The gas leaving catalysis section 38 enters second adsorption section 42 for the removal of the water vapour generated in section 38. Adsorbents used in the second adsorption section 42 can be the same as the adsorbents used in adsorption section 34, namely activated alumina, silica gel, zeolites or combinations thereof.

The purified gas, which now generally contains no more than about one ppm oxygen and no more than about one ppm moisture, is discharged from treatment vessel 30 through line 46 and valve 58 to line 62 where it is sent to storage or to further processing, such as cryogenic distillation as is illustrated in Figure 2 of the accompanying drawings.

At the same time that treatment zone 29 is purifying the gas feed, treatment zone 31 is undergoing regeneration to desorb accumulated gaseous impurities. Treatment vessel 32 is essentially the same as treatment vessel 30 and contains a corresponding first adsorption section 36, a catalysis section 40 and a second adsorption section 44. The structure of sections 36, 40 and 44 and the materials contained therein are the same as described above for sections 34, 38 and 42, respectively.

After purifying the feed gas for a period of time, each of the first and second adsorption sections 36 and 44 become contaminated with water and other impurities. Catalysis section 40 may coincidentally accumulate small amounts of moisture and also hydrogen. The gaseous impurities are removed from the beds by purging vessel 32 with a gas which does not adversely affect the catalyst and is free of oxygen and the impurities that are to be removed from vessel 32. When ultra high purity argon is being produced by the process of the invention the vessels being regenerated can be initially purged with nitrogen and subsequently purged with purified argon to minimise loss of purified argon product. A suitable purge gas is the purified product gas. Non-gaseous impurities, such as phosphorus and molybdenum compounds are retained on the first adsorbent bed. These can be permitted to accumulate on this bed for a considerable period of time before it is necessary to replace the bed.

Prior to introduction of the purge gas, vessel 32 is vented to reduce the pressure therein to close to atmospheric pressure. This is carried out by opening valve 26 thereby venting the vessel through lines 22 and 28. Referring further to FIG. 1, a purge gas obtained from an independent source (not shown), such as a side stream from line 62 or another stream free of impurities, is introduced into the system via line 70, preferably at a pressure of about 1-5 psig. Optional blower 68 may be included in the purge gas supply line to raise the pressure of the purge gas, if desired.

The temperature of the purge gas entering the system through line 70 is generally close to that of the feed gas. Therefore, in the temperature swing embodiment the purge gas is heated in heater 64, preferably to a temperature of from about 80° to 250°C. The heated regeneration gas then passes through line 54, valve 52 line 48 and into vessel 32. After purging vessel 32 the purge gas exits the system through valve 26 and line 28, thereby removing previously adsorbed impurities from the system.

The heat supplied to vessel 32 by the purge gas need only be sufficient to desorb the impurities contained therein. Accordingly, it is preferable to turn off heater 64 after sufficient heat has been introduced into vessel 32 to satisfactorily purge this vessel. The amount of heat required for a given vessel can be routinely determined. Purge gas is permitted to continue flowing through vessel 32 after heater 64 has been turned off to cool vessel 32 in preparation for the next purification step. After vessel 32 is cooled sufficiently, it is slowly repressurised by passing feed gas through open valve 18 and line 22 and into vessel 32. Vessel 30 continues to purify feed gas during this period. After repressurisation of vessel 32, feed gas is purified in this vessel, while vessel 30 undergoes the steps of venting, heating with purge gas and cooling with purge gas, as described above, for vessel 32. The process can run continuously in this manner.

The complete cycle time for the temperature-swing embodiment described in FIG. 2 normally is from about 8 to 24 hours. A complete cycle for a two-bed process operated in the temperature-swing embodiment is given in TABLE I below.

TABLE I

Step		Valves Open	Typical Time(hours)
a.	Pressurise vessel 30 with feed, purify using vessel 32	16,18,60	0.25
b.	Purify using vessel 30, vent vessel 32 to atmosphere	16,26,58	0.25
c.	Purify using vessel 30, regenerates vessel 32 with hot purge gas	16,26,52,58	2.5
d.	Purify using vessel 30, cool vessel 32 with purge gas	16,26,52,58	5.0
e.	Purify using vessel 30, pressurise vessel 32 with feed	16,18,58	0.25
f.	Purify using vessel 32, vent vessel 30 to atmosphere	18,24,60	0.25
g.	Purify using vessel 32, regenerate vessel 30 with hot purge gas	18,24,50,60	2.5
h.	Purify using vessel 32, cool vessel 30 with purge gas	18,24,50,60	5.0
		Total Time	8.0

As previously described, the purge gas used should be free of the impurities to be removed by the system (i.e. oxygen and moisture), and should contain no component that will adversely affect the materials in the three sections of the treatment vessels.

Operation of the process in the pressure-swing embodiment, wherein purge gas is nearly at the same temperature as the feed gas, is similar to the operation of the system according to the temperature-swing embodiment. The temperature of the feed gas entering the treatment zones 29 and 31 through line 14 is generally in the range of about 5°C to about 70°C and is preferably in the range of about 10° C. to about 50°C. The purge gas enters the system at line 70 and, if necessary, its pressure is raised using optional blower 68. Heater 64 is not required in the pressure-swing mode of operation. Assuming vessel 32 is undergoing regeneration, purge gas enters vessel 32 via line 54, open valve 52 and line 48, and exits vessel 32 via open valve 26 and line 28. The regeneration procedure for vessel 30 is identical to that for vessel 32.

The time for completing a cycle in the pressure-swing embodiment of the invention is typically from about 6 to 40 minutes. The cycle for the two-vessel process described in FIG. 1 is shown in TABLE II.

TABLE II

Step		Valves Open	Typical Time(sec)
a.	Pressurise vessel 30 with feed, purify using vessel 32	16,18,60	60
b.	Purify using vessel 30, vent vessel 32 t atmosphere	16,26,58	30
c.	Purify using vessel 30, purge vessel 32 with vessel 30 product	16,26,52,58	510
d.	Pressurise vessel 32, with feed, purify using vessel 30	16,18,58	60
e.	Purify using vessel 32, vent vessel 30 to atmosphere	18,24,60	30
f.	Purify using vessel 32, purge vessel 30 with vessel 32 product	18,24,50,60	510

Total Time: 20 minutes.

A system for transferring the purified gas to a cryogenic distillation system is shown in FIG. 2. The purified gas stream exiting the system at line 62 is cooled in exchanger 76 against the returning product streams in lines 78 and 86 and the purge gas stream in line 80. The warmed product streams in lines 72 and 74 are the products from the cryogenic separation. The cold feed gas stream in line 80 exiting exchanger 76 is further cooled in turboexpander 82 to produce a stream which is introduced into cryogenic distillation column 88 through line 86. Product streams leave column 88 through lines 78 and 84. In the case of argon purification, the purified gas entering the cryogenic section through line 62 contains nitrogen and hydrogen as impurities. These impurities, together with some argon, are removed from the system through line 74. The bottom product, obtained as pure argon, leaves the system through line 72.

FIG. 3 illustrates another preferred embodiment of the process of the invention. In the embodiment shown in FIG. 3, an inert gas, or an inert gas mixture containing 0.5-2.0% oxygen is compressed in compressor 2, is mixed with a stoichiometric excess of hydrogen, and is introduced into the system through line 4. Hydrogen and oxygen react to form water in reactor 5, which contains a suitable oxidation catalyst such as a noble metal on an inert support. A gas mixture comprising inert gas, unreacted oxygen (up to 500 vpm) and hydrogen, and the water formed in the reaction exits reactor 5 at line 6, and is cooled in aftercooler 8 to remove excess water. Entrained liquid water is removed from the gas stream in separator 12. The operation of the process of FIGURE 3 downstream of separator 12 is as described the same as the process carried out in the system of FIGURE 1.

The invention is further illustrated in the following examples in which, unless otherwise indicated, parts, percentages and ratios are on a volume basis.

EXAMPLE 1

The first adsorption section of a pilot plant scale unit similar to the unit illustrated in FIGURE 1 was charged with 20lbs. of activated alumina, the catalysis section of the unit was charged with 5 lbs. of an oxidation catalyst (0.5% by weight palladium on alumina), and the second adsorption section of the unit was charged with 2 lbs. of activated alumina. The three-section unit was preliminarily regenerated using oxygen-free and moisture-free nitrogen heated to a temperature of about 150°C at a flow rate of 5.0 standard cubic feet/min. for about 3 hours, following which the unit was cooled to a temperature of about 38°C. After completion of the regeneration phase, a water-saturated nitrogen stream at a temperature of about 38°F and a pressure of about 70 psia and containing 1.5 volume percent hydrogen and 1.0 vpm oxygen was passed through the unit at a flow rate of 12 standard cubic feet/min. The unit was operated according to the cycle set forth in TABLE III.

TABLE III

Step	Time (hr.)
Vessel Pressurisation	0.1
Feed purification	3.0
Vessel venting	0.1
Heating with impurity-free nitrogen	1.6
Cooling with impurity-free nitrogen	1.2
Total	6.0

The run was permitted to continue for several 6 hour cycles. During the purification phase of the cycle, the gas exiting the unit was continuously analysed for oxygen and moisture content. The above procedure was repeated using water-saturated nitrogen gas streams containing 15.0, 30.0, 60.0 and 90.0 vpm oxygen. The results of these experiments are tabulated in TABLE IV.

TABLE IV

Run	O_2 Conc. in Feed Gas, vpm	O_2 Conc. in Product Gas, vpm	H_2O Conc. in Product gas, vpm
1	1.0	<0.1	<0.1
2	15.0	<0.1	<0.1
3	30.0	<0.1	<0.1
4	60.0	<0.1	<0.1
5	90.0	<0.1	<0.1

EXAMPLE 2 (Comparative)

The following example shows the adverse effect of moisture on the oxidation catalyst. The pilot plant unit described in Example 1 was preliminarily regenerated in the manner described in Example 1. A water saturated nitrogen stream having a temperature of 38°C and a pressure of 70 psia, and containing 1.5 vol. percent hydrogen and 30 vpm oxygen was passed through the unit at a flow rate of 12 standard cubic feet/min. The gas stream was permitted to flow through the unit for several hours During the first four hours of the purification phase, the oxygen and water concentrations in the product gas stream were less than 0.1 vpm. However, the water and oxygen concentration in the product began to increase after 4 hours of purification, and at the end of 8 hours the oxygen and water concentrations in the product gas stream were greater than 2 vpm and several hundred vpm, respectively.

The above examples illustrated the benefits of the invention. In Example 1, in which the catalyst bed was

maintained substantially anhydrous by continuously removing moisture from the gas stream prior to its entry into the catalysis section, a product gas containing less than 0.1 vpm oxygen and less than 0.1 vpm water was continuously produced. On the other hand, in the process of Example 2, in which the catalyst bed was not maintained anhydrous, the effectiveness of the catalyst bed gradually deteriorated.

For instance, oxidation catalysts other than noble metal catalysts can be used and adsorbents other than alumina can be used in the process of the invention. The scope of the invention is limited only by the breadth of the appended claims. Inert gases other than argon and nitrogen can be purified.

Claims

1. A process for the removal of oxygen from an inert gas stream containing oxygen impurity comprising:
   a) introducing hydrogen into the inert gas stream to the extent necessary to ensure that the gas stream contains at least sufficient hydrogen to enable all of the oxygen in the gas stream to be converted to water;
   b) contacting the inert gas stream with an oxidation catalyst in a first catalysis zone, thereby reacting a substantial amount of the oxygen in the stream with hydrogen to form water;
   c) cooling the gaseous effluent from said first catalysis zone;
   d) contacting the cooled gaseous effluent with an adsorbent in a first adsorption zone, thereby removing substantially all of the water contained in the cooled gaseous effluent characterised by
   e) contacting the substantially anhydrous effluent from said first adsorption zone with an oxidation catalyst in a second catalysis zone, thereby combining substantially all of the oxygen in said substantially anhydrous effluent with hydrogen to produce water; and
   f) contacting the gaseous effluent from said second catalysis zone with an adsorbent in a second adsorption zone, thereby producing a purified gas stream containing not more than about 1 vpm of oxygen, and not more than about 1 vpm water.

2. A process according to Claim 1, wherein the said inert gas stream contains up to 3% by volume of oxygen.

3. A process according to claim 1 or claim 2, wherein the concentration of oxygen present in the gaseous effluent from said first catalysis zone is not greater than about 500 vpm.

4. A process according to any one of the preceding claims, wherein the said inert gas is argon.

5. A process according to claim 4, in which the argon is produced by cryogenic air separation.

6. A process according to claim 5, in which the purified inert gas stream is distilled to remove residual hydrogen and/or nitrogen impurities therefrom.

7. A process according to any one of the preceding claims, in which the upstream end of the second catalysis zone is continuous to the first adsorption zone and the downstream end of the second catalysis zone is contiguous to the second adsorption zone.

8. A process according to any one of the preceding claims, additionally including as step (g) regenerating said first and second adsorption zones by passing a substantially oxygen-free and moisture free gas stream therethrough thereby removing water therefrom.

9. A process according to claim 8, in which while step (g) is being performed in a first group of first and second adsorption zones, steps (d) to (f) are being performed in a second group of first and second adsorption zones.

10. Apparatus for purifying an inert gas stream including oxygen impurity, comprising:
    (i) a first catalytic reaction zone for reacting the oxygen impurity in the inert gas stream with hydrogen to form a partially purified gas stream comprising said inert gas, residual oxygen impurity and water;
    (ii) means for cooling the partially purified inert gas stream; and
    (iii) a first adsorption zone for adsorbing said water from the cooled gas stream;
    characterised in that the apparatus additionally includes downstream of said adsorption zone;
    (iv) a second reaction zone for reacting with hydrogen the residual oxygen in the partially purified inert gas stream to form water; and

(v) a second adsorption zone for adsorbing water formed in the first reaction zone, whereby a purified inert gas stream essentially free of water vapour and oxygen is able to be produced.

11. Apparatus as claimed in claim 10, wherein said first and second adsorption zones and said first reaction zone are all defined in the same vessel.

12. Apparatus as claimed in claim 10 or claim 11, wherein the source of said inert gas stream including oxygen impurity is a distillation column for separating oxygen from argon.

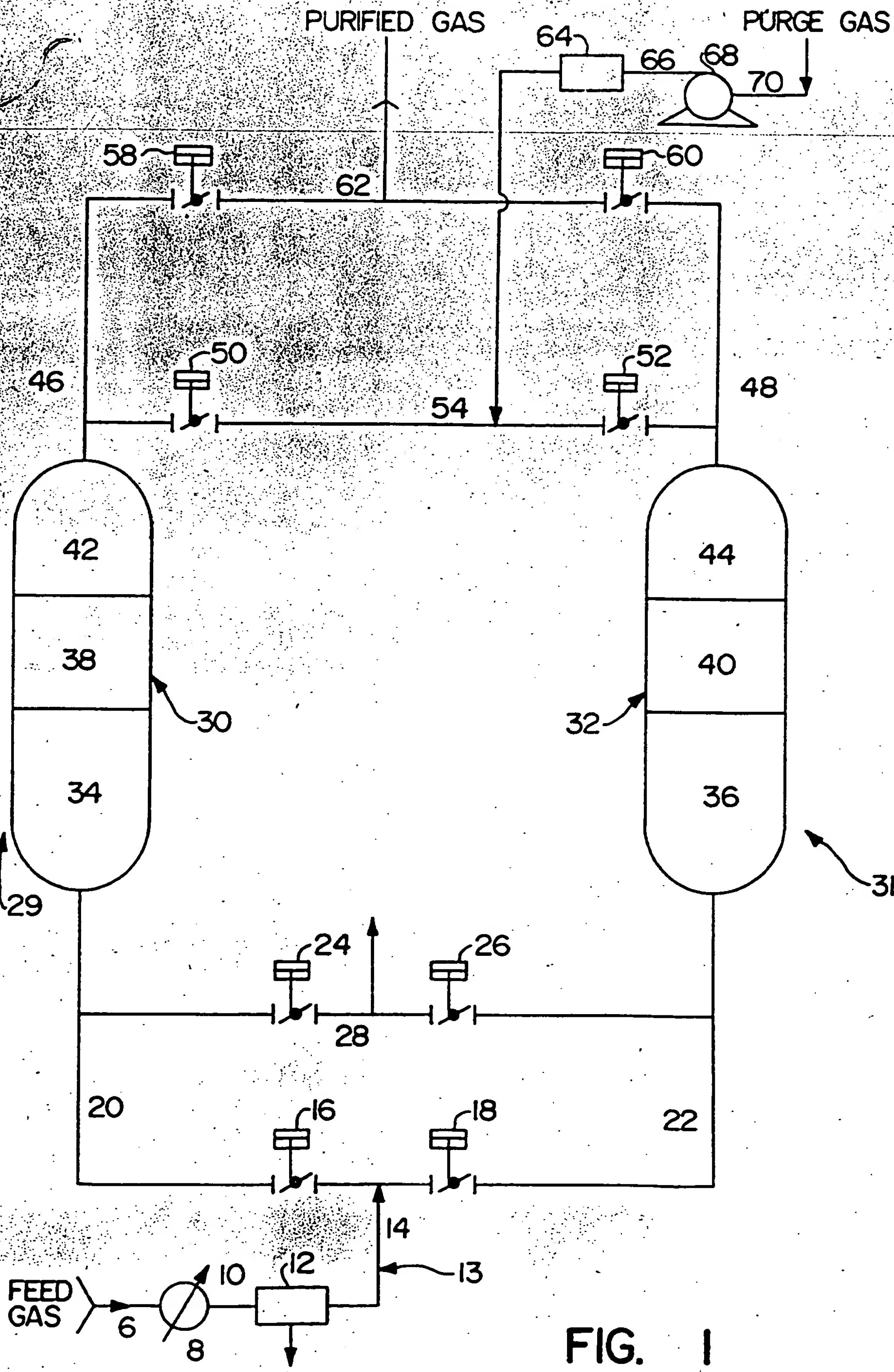
PURIFIED GAS
PURGE GAS
64
66
68
70
58
60
62
50
52
46
48
54
42
38
34
30
29
44
40
36
32
31
24
26
28
20
22
16
18
14
13
12
10
FEED GAS
6
8

FIG. 1

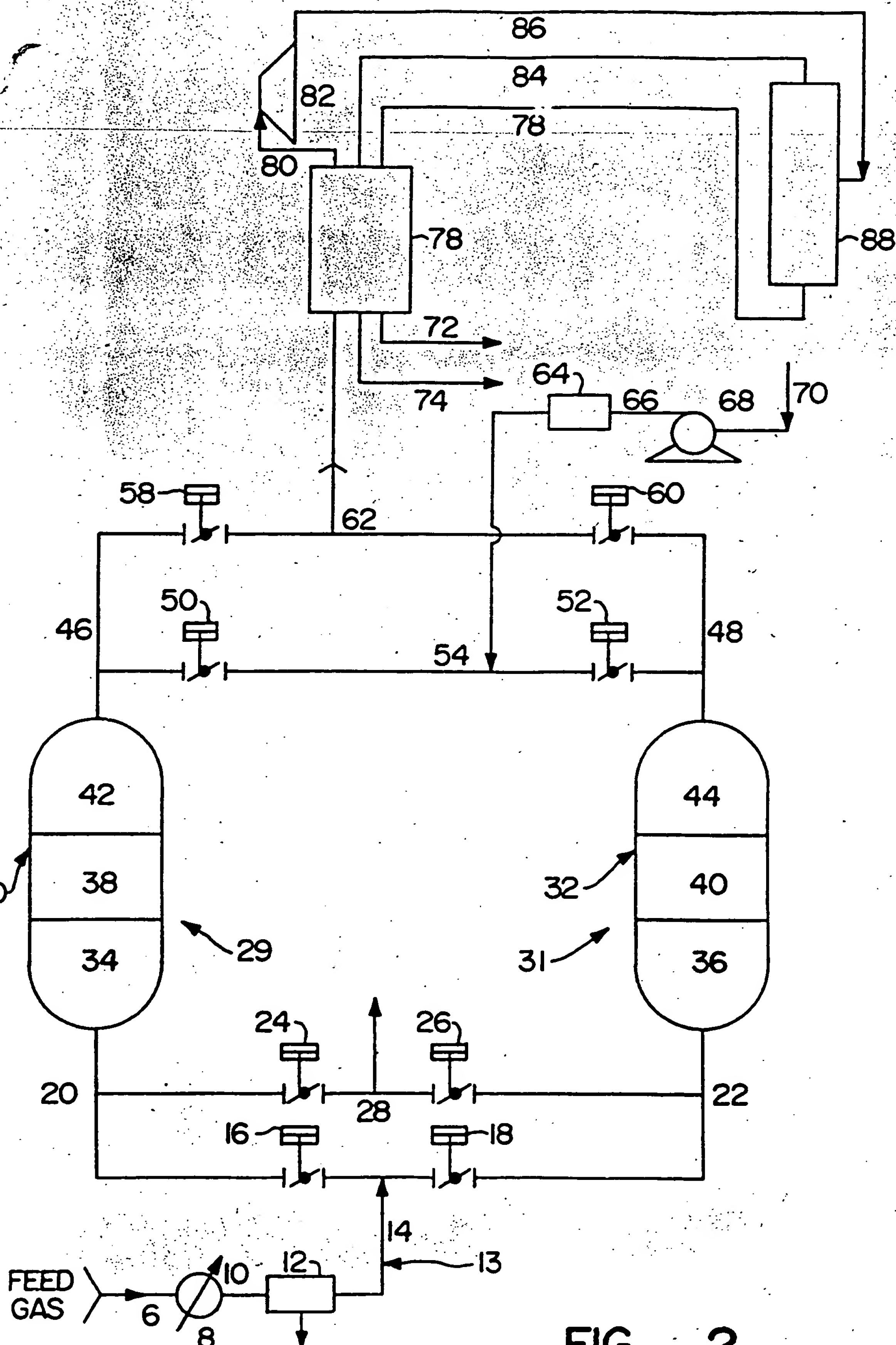
86
84
82
78
80
78
88
72
74
64
66
68
70
58
60
62
50
52
46
48
54
42
44
38
40
30
32
34
36
29
31
24
26
20
22
28
16
18
14
13
12
10
FEED GAS
6
8

FIG. 2

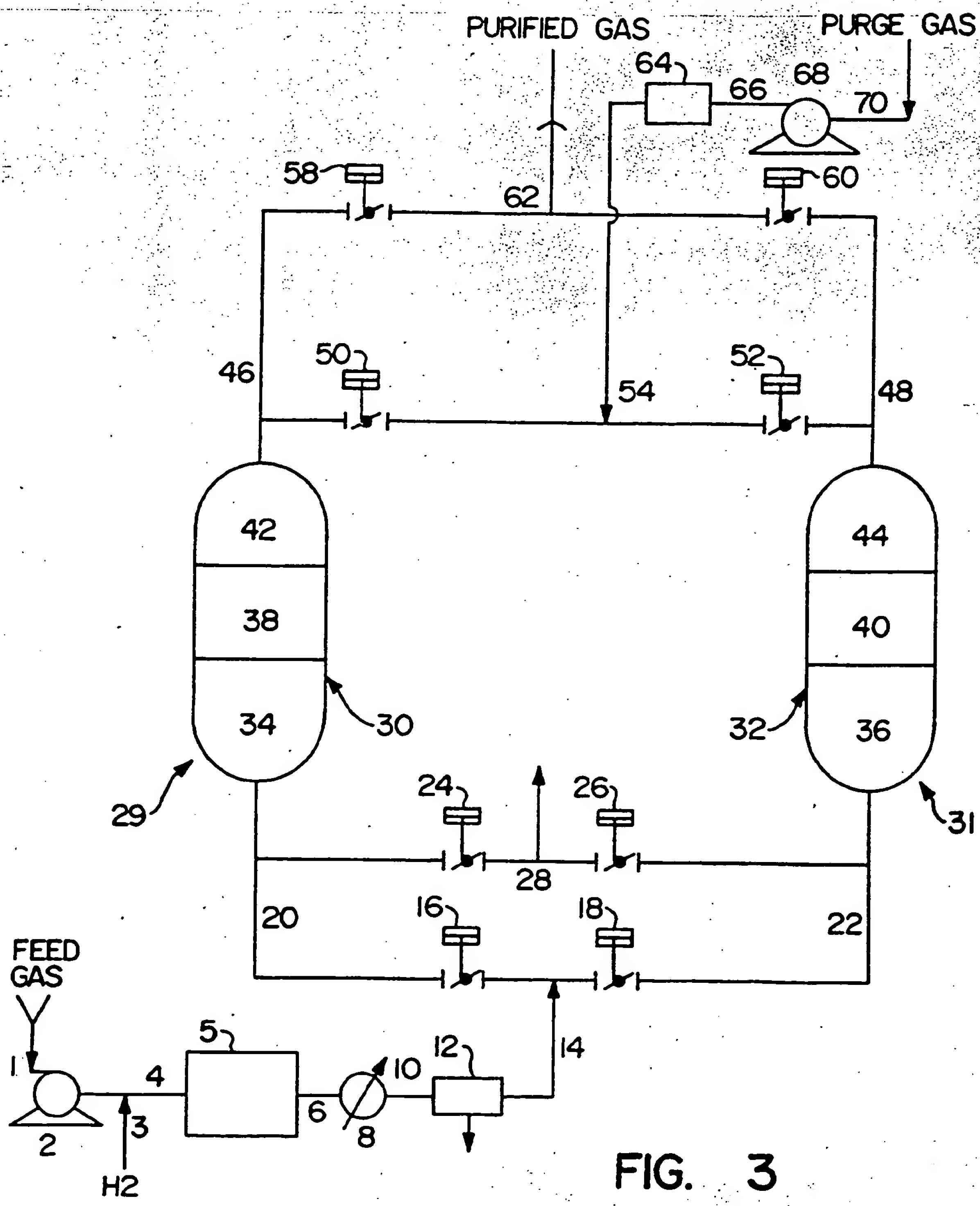
PURIFIED GAS
PURGE GAS
64
66
68
70
58
60
62
46
50
52
54
48
42
38
34
30
44
40
36
32
29
31
24
26
28
20
16
18
22
FEED GAS
1
2
3
H2
4
5
6
8
10
12
14

FIG. 3

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 92 30 4807

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
D,Y A	US-A-3 535 074 (NAKASHIMA) * column 1, line 23 - line 27 * * column 4, line 67 - column 6, line 21; claim 1; figures 1,2; example 1 * ---	1,10 2,4-6,12	C01B23/00 C01B21/04 B01D53/04
P,Y A	EP-A-0 438 282 (THE BOC GROUP, INC.) * claims 1,5,8,10-12; figures 1-3 * ---	1,10 7-9,11	
A	DE-A-3 401 197 (BASF AG) * the whole document * ---	1-4,10	
A	CHEMICAL ABSTRACTS, vol. 101, no. 12, September 1984, Columbus, Ohio, US; abstract no. 93654H, BARABASH ET AL.: 'CATALYTIC AND ADSORPTION CHEMICAL PURIFICATION OF INERT GASES, HYDROGEN AND METHANE FOR THE REMOVAL OF OXYGEN' page 149 ; * abstract * ---	1,3,4	TECHNICAL FIELDS SEARCHED (Int. Cl.5)
A	DE-A-3 915 003 (GEBRUEDER HAMMER GMBH) * the whole document * -----	1,10	C01B B01D F25J

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	10 AUGUST 1992	CUBAS ALCARAZ J.L.

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document